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## Large magnetocaloric effect of NdGa compound due to successive magnetic transitions

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The magnetic behavior and MCE property of NdGa compound were studied in detail. According to the temperature dependence of magnetization (M-T) curve at 0.01 T, two sharp changes were observed at 20 K ( $T_{SR}$ ) and 42 K ( $T_C$ ), respectively, corresponding to spin reorientation and FM-PM transition. Isothermal magnetization curves up to 5 T at different temperatures were measured and magnetic entropy change ( $\Delta S_M$ ) was calculated based on M-H data. Temperature dependences of  $-\Delta S_M$  for a field change of 0-2 T and 0-5 T show that there are two peaks on the curves corresponding to  $T_{SR}$  and  $T_C$ , respectively. The value of the two peaks is 6.4 J/kg K and 15.5 J/kg K for the field change of 0-5 T. Since the two peaks are close, the value of  $-\Delta S_M$  in the temperature range between  $T_{SR}$  and  $T_C$  keeps a large value. The excellent MCE performance of NdGa compound benefits from the existence of two successive magnetic transitions. © 2018 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). <https://doi.org/10.1063/1.5006506>

### I. INTRODUCTION

Magnetic refrigeration, which is based on magnetocaloric effect (MCE), is expected to be a promising alternative to the conventional gas compression refrigeration because of its higher energy efficiency and friendly environment.<sup>1-5</sup> To improve the application of this cooling technology, many efforts have been made to explore advanced MCE materials. The performance of MCE materials is usually evaluated by magnetic entropy change ( $\Delta S_M$ ), refrigeration temperature width ( $\delta T_{FWHM}$ ) and refrigeration capacity (RC). Lots of MCE materials with large value of  $\Delta S_M$  have been obtained and studied in room temperature range.<sup>6-13</sup> In recent years, lots of attention have also been paid on the magnetic materials with low transition temperatures, for this kind of MCE materials can be used for liquefaction,<sup>14,15</sup> such as TmZn,<sup>16</sup> RNi (R=Ho, Er),<sup>17,18</sup> R<sub>12</sub>Co<sub>7</sub> (R=Ho, Er)<sup>19-23</sup> and HoCoSi.<sup>24</sup> Especially the magnetic compounds with successive transitions show advantage on  $\delta T_{FWHM}$  and RC and thus researchers are inclined to explore MCE materials in those with several magnetic transitions.

Binary RGa (R=rare-earth) intermetallic compounds show interesting magnetic properties according to the investigation of the magnetic structures by employing Mossbauer spectroscopy experiment<sup>25</sup> and Neutron diffraction experiment.<sup>26-28</sup> It was observed that the RGa (R=Gd, Nd, Sm, Ho and Er) compounds exhibit spin-reorientation (SR) transition below  $T_C$ .<sup>25</sup> Thereafter people

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studied the magnetic and MCE properties of  $R\text{Ga}$  ( $R=\text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}$ ) compounds.<sup>29–32</sup> Furthermore, the  $\delta T_{\text{FWHM}}$  of  $\text{ErGa}$  compound was extended successfully by spin optimization.<sup>33</sup> In addition, interesting magnetic properties, transport properties and MCEs were also found in  $\text{TmGa}$  and  $\text{PrGa}$  compounds.<sup>34–37</sup> In this paper, we investigate the magnetic properties and MCEs of  $\text{NdGa}$  compound. The correlations between MCE and magnetic transitions will be discussed.

## II. EXPERIMENT

The  $\text{NdGa}$  ingots were prepared in a purified Ar atmosphere by arc-melting of the stoichiometric amounts of the high purity (>99.9 wt. %) constituent elements on a water cooled copper hearth. To achieve compositional homogeneity, the obtained ingot was wrapped in a molybdenum foil, sealed in a high-vacuum quartz tube, annealed at  $800^\circ\text{C}$  for 7 days and then quenched into liquid nitrogen. The phase structure and the crystal lattice parameters were examined by the Rietveld refinement of the room-temperature x-ray powder diffraction (XRD) data collected using the  $\text{Cu } K\alpha$  radiation. Magnetization measurements were carried out as functions of temperature and magnetic field by using a superconducting quantum interference device (SQUID) magnetometer.

## III. RESULTS AND DISCUSSION

The XRD pattern of  $\text{NdGa}$  compound was obtained at room temperature and then the pattern was fitted by Rietveld analysis method. Results show that the prepared compound is of single phase, crystallizing in the orthorhombic  $\text{CrB}$ -type structure (space group  $\text{Cmcm}$ ) in agreement with the previous reports.<sup>25,38–40</sup> The structure can be described as the stacking of triangular prisms with rare-earth atoms at the corners and the gallium atoms nearly at the center.  $R$  atoms and Ga atoms occupy two different  $4c$  ( $0, y, 1/4$ ) equivalent sites.<sup>40</sup> The lattice parameter was compared with other  $R\text{Ga}$  ( $R=\text{Pr}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}$  and  $\text{Tm}$ ) compounds. Lattice parameters decrease continuously with the  $R$  atom sweeping from Pr to Tm due to the constriction of radius for  $R$  atoms.

Both temperature dependences of zero-field-cooling (ZFC) and field-cooling (FC) curves under a magnetic field of 0.01 T for  $\text{NdGa}$  compound, which are shown in Fig. 1. As temperature increases,  $\text{NdGa}$  compound undergoes two abrupt changes, which are corresponding to spin-reorientation (SR) transition and ferromagnetic (FM) to paramagnetic (PM) transition, respectively. The SR transition temperature ( $T_{\text{SR}}$ ) and Curie temperature ( $T_{\text{C}}$ ) are determined to be 20 K and 42 K, respectively, according to the derivative curve of FC. The values of transition temperatures observed here are in good agreement with the previous results.<sup>25</sup> As temperature decreases, the magnetization shows a decrease when it scans over 20 K. The ZFC curve shows a characteristic similar to compensation effect in ferrimagnetic materials. All the above information indicates complex magnetic structure may exist and complex magnetic transition occurs. No thermal hysteresis is observed at the temperatures above  $T_{\text{C}}$  according to the ZFC and FC curves. However, obvious thermal irreversibility is observed in the

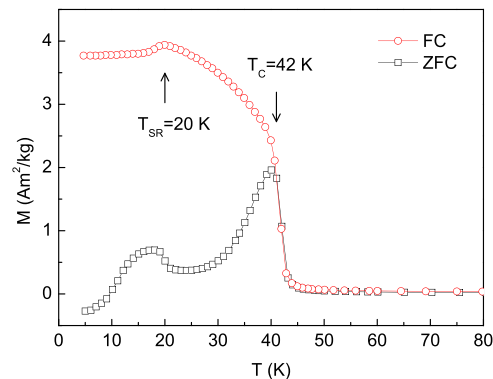


FIG. 1. Temperature dependences of zero-field-cooling and field-cooling magnetizations for  $\text{NdGa}$  compound at a magnetic field of 0.01 T.

temperature range below  $T_C$  as observed in ErGa compound<sup>29</sup> and it is likely due to a domain wall pinning effect.

In order to study the magnetic properties of NdGa compound, magnetization isotherms were measured from 5 K to 74 K under applied fields up to 5 T. The M-H curves at different temperatures are shown in Fig. 2(a) and the enlarged view of M-H curves at low temperatures are shown in Fig. 2(b). It is observed that the magnetization goes up with magnetic field increasing and reaches saturation value when the field is large enough. When the M-H curves at low temperatures are shown in an enlarged view, it is found that the magnetization firstly increases slowly with field, and then it goes up quickly when magnetic field exceeds critical value. The linear relationship between M and H in low field range means the existence of antiferromagnetic (AFM) ground state. The sharp increase of magnetization indicates that metamagnetic transition from AFM to FM occurs. As temperature increases, the critical field is getting smaller and smaller. When temperature goes up over 21 K, the M-H curves show typical FM characteristic. That is to say, the magnetic transition at 20 K in M-T curve is corresponding to AFM to FM type spin reorientation. NdGa compound still shows FM characteristic at the temperatures above  $T_C$  indicating the existence of short range FM order as has been observed ErGa compound.<sup>29</sup>

The  $\Delta S_M$  of NdGa compound was calculated on basis of isothermal magnetization data by using the Maxwell relation  $\Delta S_M = \int_0^H (\partial M / \partial T)_H dH$ . The temperature dependences of  $\Delta S_M$  are shown in Fig. 3. There are two sharp peaks on the  $\Delta S_M$ - $T$  curves around  $T_{SR}$  and  $T_C$ , respectively. It indicates that there are large variations of magnetic order in the process of AFM to FM transition and FM to PM transition. That is to say, both types of magnetic transitions contribute to MCE, which has been observed in other RGa (R=Gd, Tb, Dy, Ho, Er) compounds.<sup>26,29,30,32,33</sup> Analysis of Mössbauer spectra has shown that the rotation of the magnetic moments occurs in the ac-plane at low temperatures due to the competition between the exchange interaction and the interaction of the crystalline electric field in NdGa compound.<sup>25,29</sup> For polycrystalline NdGa compound, the applying of magnetic field will destroy the balance mentioned above. It is the most dramatic temperature zone that the magnetic order changes around  $T_{SR}$ , thus noticeable magnetic entropy changes were observed around  $T_{SR}$ .

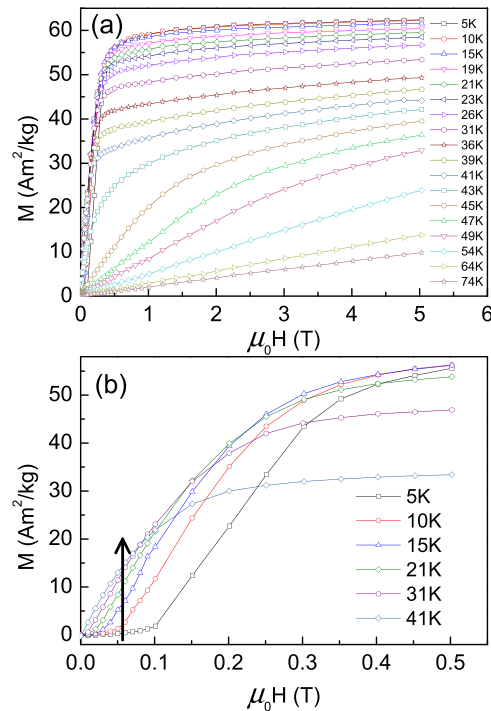


FIG. 2. (a) Isothermal magnetization curves for NdGa compound in a wide temperature range with applied fields up to 5 T. (b) The enlarged view of selected M-H curves.

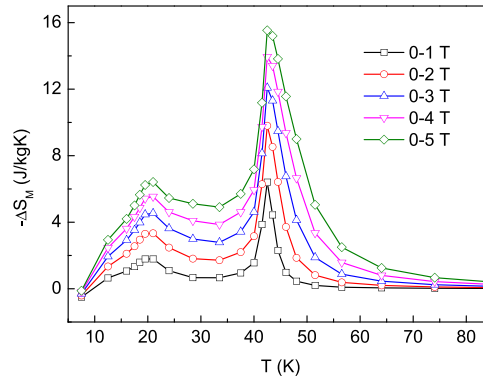


FIG. 3. Magnetic entropy change ( $\Delta S_M$ ) as a function of temperature for NdGa compound under field changes of 0-1 T, 0-2 T, 0-3 T, 0-4 T and 0-5 T, respectively.

The maximal values of  $-\Delta S_M$  are 6.4 and 15.5 J/kg K at  $T_{SR}$  and  $T_C$  for a field change of 0–5 T, respectively. The values of  $-\Delta S_M$  is smaller than that of ErGa and HoGa compounds,<sup>26,29</sup> but that is larger than TbGa and DyGa.<sup>32</sup> In addition, it is noted that the  $-\Delta S_M$  is negative at 7.5 K, which is the typical result of AFM ground state as has been observed in other AFM materials.<sup>41,42</sup> Since there are two peaks on the  $\Delta S_M$  curves and one overlaps the other, the  $\Delta S_M$  almost keeps a constant value in a wide range of temperatures. Although the value of  $\Delta S_M$  at low temperatures is only one third of the peak value around  $T_C$ , a plateau is obtained on the  $\Delta S_M$  curve of NdGa compound. The RC of NdGa compound was estimated based on the  $\Delta S_M-T$  curves by using the approach suggested by Gschneidner *et al.*<sup>43</sup> The RC value is defined as  $RC = \int_{T_1}^{T_2} |\Delta S_M| dT$ , where  $T_1$  and  $T_2$  are the temperatures corresponding to both sides of the half-maximum value of  $\Delta S_M$  peak, respectively. And the refrigerant temperature width ( $\delta T_{FWHM}$ ) is determined as  $T_2 - T_1$ . It is important to note that  $T_1$  is corresponding to the peak around  $T_{SR}$  and  $T_2$  is corresponding to the peak around  $T_C$  for NdGa compound. The value of RC is calculated to be 96.5 J/kg and 249.8 J/kg for a field change of 0-2 T and 0-5 T, respectively. The value of  $\delta T_{FWHM}$  is calculated to be 31.4 K and 36.3 K for a field change of 0-2 T and 0-5 T, respectively. Though the  $\Delta S_M$  is smaller than ErGa compound, the refrigerant capacity is larger than ErGa compound (22.6 K for 0-2 T, 30.9 K for 0-5 T).<sup>29</sup> The large  $\delta T_{FWHM}$  of NdGa originates from the combined contribution from SR and FM-PM transitions.

#### IV. CONCLUSIONS

NdGa compound undergoes an SR magnetic transition at 20 K and an FM-PM transition at 42 K with temperature increasing. The SR in NdGa compound is AFM-FM type magnetic transition. Good thermal reversibility is observed in the temperature range above  $T_C$ , where short range FM order also exists. Two peaks are observed on the  $-\Delta S_M$  curves corresponding to  $T_{SR}$  and  $T_C$ , respectively. The maximal values are 6.4 and 15.5 J/kg K for a field change of 0–5 T at the transition temperatures respectively. The excellent MCE performance makes NdGa compound competitive refrigerant material used in low temperature zone.

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